FORMATION OF N-METHYL-2-NITROSO-4,6-DINITROANILINE FROM METHYL ESTER OF N-METHYL-N-(2,4,6-TRINITROPHENYL)GLYCINE

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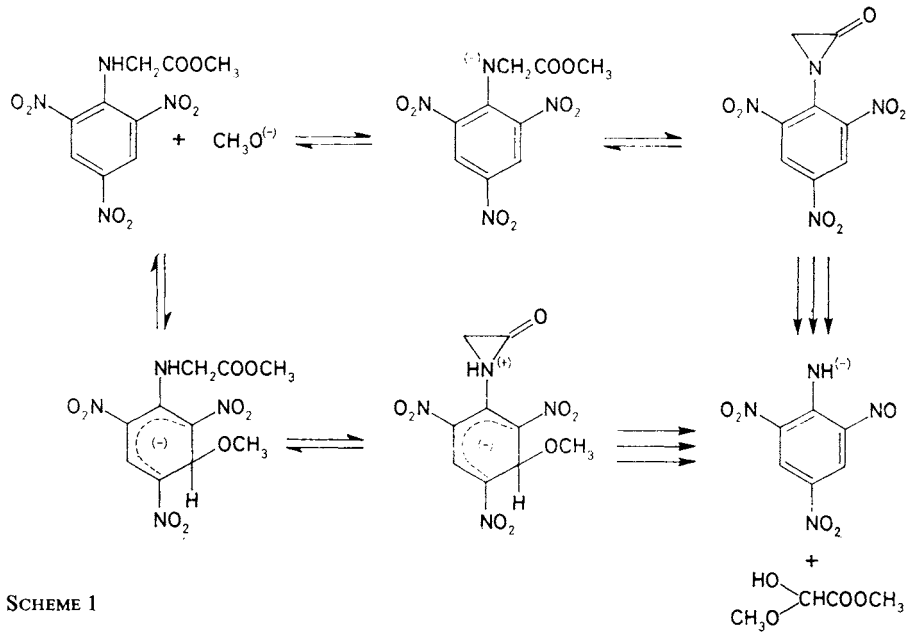
Received July 27th, 1987

The reaction of methyl ester of N-methyl-N-(2,4,6-trinitrophenyl)glycine with methoxide in methanol produces N-methyl-2-nitroso-4,6-dinitroaniline. The kinetics of formation of the nitroso compound have been studied, and a mechanism of its formation has been suggested consisting in the intramolecular attack of CH_2 group of aziridinone intermediate by oxygen atom of nitro group and in subsequent E2 elimination reaction. The aziridinone intermediate is formed by the attack of carbon atom of carboxylic group of 1,3-adduct of the starting ester with methoxide by the formally electroneutral tertiary nitrogen. In methoxide solution, N-methyl-2-nitroso-4,6-dinitroaniline undergoes another reduction-oxidation reaction giving 2-amino-2′-methylamino-3,3′,5,5′-tetranitroazoxybenzene.

Our previous paper[1] dealt with the reaction of methyl and ethyl esters of N-(2,4,6-trinitrophenyl)glycine with methoxide ion. This reaction gave 2-nitroso-4,6-dinitro-



SCHEME 1

aniline (*I*) in a yield of 75%. The product structure was proved by means of ^1H, ^{13}C, and ^{15}N NMR and mass spectra and elemental analysis. At the concentrations used for spectral measurements (about 10^{-4} mol l^{-1}) the nitroso compound *I* is formed quantitatively. A mechanism of formation of the nitroso compound *I* was suggested on the basis of kinetic studies of the reactions of esters and methylamide of N-(2,4,6-trinitrophenyl)glycine and methyl and ethyl esters of N-(2,4,6-trinitrophenyl)alanine. Besides the formation of nitroso compound *I* from conjugated base of the substrate, an alternative way of formation of aziridinone from 1,3-adduct of the substrate with methoxide was also considered (Scheme 1).

In order to find the extent to which the reaction via the 1,3-adduct is real, we decided to study the reaction of methyl ester of N-methyl-N-(2,4,6-trinitrophenyl)-glycine with mehoxide. In this case the reaction with methoxide cannot lead to the conjugated base of the substrate, and the way to the nitroso compound would have to go through the 1,3-adduct with methoxide.

EXPERIMENTAL

The ^1H, ^{13}C, *and* ^{15}N NMR *spectra* were measured with a JNM FX-100 spectrometer (JEOL) at 99·602, 25·047, and 10·095 MHz, respectively. An about 10% solution of compound *II* in hexadeuteriodimethyl sulphoxide and a saturated solution of compound *III* in deuteriochloroform were used for the measurements. The chemical shifts $\delta(^1H)$ are related to hexamethyldisiloxane (δ 0·05), the chemical shifts $\delta(^{13}C)$ to the middle signal of the solvent multiplet(δ 39·6 for hexadeuteriodimethyl sulphoxide and δ 77·0 for deuteriochloroform), and the chemical shifts $\delta(^{15}N)$ to neat external $CH_3{}^{15}NO_2$ (δ 0·0, negative values denote upfield shifts). The ^1H and ^{13}C NMR spectra of 2-amino-2′-methylamino-3,3′,5,5′-tetranitroazoxybenzene were measured with an AM-400 Bruker spectrometer at 400·13 and 100·62 MHz, respectively. N-Methyl-N-(2,4,6-trinitrophenyl)glycine methyl ester (*II*) was prepared by the reaction of 1-chloro-2,4,6-trinitrobenzene with hydrochloride of sarcosine methyl ester by a procedure described[1] for preparation of N-(2,4,6-trinitrophenyl)glycine methyl ester. Yield 83%, m.p. 92·5–94·5°C (benzene–cyclohexane). For $C_{10}H_{10}N_4O_8$ (314·2) calculated: 38·23% C, 3·21% H, 17·83% N; found: 38·11% C, 3·33% H, 17·83% N. ^1H NMR ($(C^2H_3)_2SO$): 8·94 s, 2 H (Pi); 4·02 s, 2 H (CH_2); 3·71 s, 3 H (OCH_3); 3·00 s, 3 H (NCH_3). ^{13}C NMR ($(C^2H_3)_2SO$): 168·48 (CO), 138·88 (C-1), 144·03 (C-2, 6), 125·31 (C-3, 5), 142·63 (C-4), 55·74 (CH_2), 52·11 (OCH_3), 41·18 (NCH_3). N-Methyl-N-(2-^{15}N-nitro-4,6-dinitrophenyl)glycine methyl ester was prepared from 1-chloro-2-^{15}N-nitro-4,6-dinitrobenzene, which was prepared[2] by the reaction of 2-^{15}N-nitro-4,6-dinitrophenol with $POCl_3$. 2-^{15}N-Nitro-4,6-dinitrophenol was prepared by nitration[3] of 2,4-dinitrophenol with $H^{15}NO_3$ (60% HNO_3, 10% ^{15}N). The ^1H NMR spectrum was identical with that of the non-labelled ester.

N-*Methyl*-2-*nitroso*-4,6-*dinitroaniline* (III): A stirred solution of 4 g (12·7 mmol) N-methyl-N-(2,4,6-trinitrophenyl)glycine methyl ester in 120 ml methanol was treated with 16 ml 1 mol l^{-1} sodium methoxide solution added at once and followed, after 10 s, by 4 ml (70 mmol) acetic acid in 10 ml methanol. After 1·5 h, 0·55 g orange substance was collected by suction. The methanolic filtrate was diluted with c. 300 ml saturated sodium chloride solution, and the product was extracted with 500 ml ethyl acetae. The extract was shaken with saturated NaCl solution, dried with Na_2SO_4, and the solvent was removed by vacuum distillation at room temperature. The

evaporation residue was immediately dissolved in chloroform and submitted to column chromatography (silica gel, 240 mm length, 30 mm diameter, chloroform as the eluent). The fraction containing the nitroso compound *III* was rid of the solvent by vacuum distillation to give 1·65 g product (57·3%), m.p. 93–96°C (partial decomposition). For $C_7H_6N_4O_5$ (226·2) calculated: 37·18% C, 2·67% H, 24·77% N; found: 37·52% C, 2·92% H, 24·73% N. ^{1}H NMR (C^2HCl_3, 60°C): 9·99 b, 1 H (NH); 9·26 d, 1 H (H-5, $J(3, 5) = 2·93$ Hz); 7·24 bd, 1 H (H-3); 3·73 d, 3 H (CH_3, $J = 5·38$ Hz). ^{13}C NMR (C^2HCl_3, 60°C): 158·24 (C-2), 149·44 (C-1), 137·11 and 134·12 (C-4 and/or C-6), 127·85 (C-5), 110·54 (C-3), 37·63 (CH_3).

The separated orange-red solid was recrystallized from dimethyl sulphoxide and washed with methanol, m.p. 265–270°C (decomp.). For $C_{13}H_{10}N_8O_9$ (422·3) calculated: 36·98% C, 2·39% H, 26·54% N; found: 37·06% C, 2·68% H, 26·25% N. ^{1}H NMR (hexadeuteriodimethyl sulphoxide, 40°C): 9·67 d, 1 H ($J = 2·66$ Hz); 8·96 m, 3 H; 8·58 b, 3 H (NH, NH_2); 2·95 d, 3 H ($J = 3·00$ Hz, $NHCH_3$). ^{13}C NMR (hexadeuteriodimethyl sulphoxide, 40°C): 146·62, 142·83, 136·55, 133·99, 133·20, 132·73, 130·44, 130·34, 127·45 (CH), 124·76 (CH), 124·43 (CH), 121·28 (CH), 30·94 (NCH_3).

The nitroso compound *III* labelled with ^{15}N at positions 2,6 was prepared in the same way from N-methyl-N-(2-^{15}N-nitro-4,6-dinitrophenyl)glycine methyl ester; yield 62%, m.p. 90 to 93°C. The ^{1}H NMR spectrum was identical with that of the non-labelled nitroso compound *III*. ^{15}N NMR (deuteriochloroform); 485·0 (NO), −13·3 (or −14·5) and −16·3 (2× NO_2), −290·1 (NH).

The kinetic measurements were carried out with a Stopped Flow Spectrophotometer Durrum D-110 at 25°C. The reaction was realized by mixing equal volumes of methanolic ester *II* ($c = (0·6$ to $1·5) \cdot 10^{-5}$ mol l^{-1}) and methanolic sodium methoxide ($3 \cdot 10^{-3}$ to $5 \cdot 10^{-1}$ mol l^{-1}). In order to find the rate constant of formation of the nitroso compound *III*, we followed the absorbance increase at 420 nm (λ_{max} of the anion of the nitroso compound) at the time scale

TABLE I

The experimental rate constants of formation of the adduct *IV* (τ_1^{-1}), of formation of the nitroso compound *III* (τ_2^{-1}), and of formation of the nitroso compound *I* (k_{exp}) in methanol at 25°C

$[CH_3O^{(-)}] \cdot 10^2$	τ_1^{-1}, s^{-1}	τ_2^{-1}, s^{-1a}	k_{exp}, s^{-1b}
0·15	—	—	0·30
0·23	37 ± 4	0·13	0·40
0·50	—	0·25	0·70
1·25	—	0·62	1·05
2·50	—	1·02	1·25
3·30	—	1·32	1·35
5·00	59 ± 9	2·10	1·40
10	82 ± 7	—	—
15	98 ± 6	—	—
20	120 ± 5	—	—
25	139 ± 11	—	—

[a] τ_2^{-1} ± 5%; [b] k_{exp} ±3%.

of 100 ms to 1 s per one division of the oscilloscope. For determination of the rate constant of formation of the equilibrium mixture of the substrate *II* and the 1,3-adduct with methoxide *IV* we measured the absorbance increase at 495 nm (the long-wave maximum in the spectrum of the adduct *IV*) at the time scale of 2 ms to 10 ms. The curve of the dependence absorbance–time was transferred from the memory of a PM 3 311 oscilloscope (Philips) to a BAK 5T recorder (ZPA Čakovice). As subsequent reactions take place in both the cases, the absorbance does not remain constant after the reaction followed is over, but it exhibits further slower changes. In the measurements of the rate of formation of the adduct *IV* as well as that of the nitroso compound *III* at $[CH_3O^{(-)}] < 0{\cdot}1$ mol l^{-1}, these changes were small and (within the time interval measured, i.e. 6—7 half-lives of the reaction studied) linear. The rate constants were calculated from the equation $(\tau_{1/2})^{-1}\, t = 2{\cdot}3 \log (A_{ext} - A_t) + \text{const.}$, where A_t denotes the absorbance at the time t, and A_{ext} is the absorbance value obtained by extrapolation of the linear section of the absorbance–time dependence (after the reaction investigated was over) to the time t. At the methoxide concentrations above 0·1 mol l^{-1}, the subsequent absorbance changes in the measurements of the rate of formation of the nitroso compound *III* were large and non-linear, hence it was impossible to find reliable $\tau_{1/2}$ values.

The reaction of N-(2,4,6-trinitrophenyl)glycine methyl ester[1] with methoxide was realized in the Stopped Flow Durrum D-110 apparatus by mixing the methanolic substrate solution with methanolic methoxide ($3 \cdot 10^{-3}$ to 10^{-1} mol l^{-1}). The substrate concentration was $4 \cdot 10^{-5}$ mol . l^{-1} and $1 \cdot 10^{-4}$ mol l^{-1} in the measurements at 400 nm (the absorbance increase) and 500 nm (the absorbance decrease), respectively. The analytical wavelength of 500 nm was used at the methoxide concentrations above 10^{-2} mol l^{-1}. The rate constants k_{exp} were obtained in the standard way from the relation $k_{exp}t = -2{\cdot}3 \log (A_t - A_\infty)$ or $k_{exp}t = -2{\cdot}3 \log . (A_\infty - A_t)$. Each measurement was repeated four times, and the average values of the rate constants are presented in Table I.

RESULTS AND DISCUSSION

After addition of sodium methoxide (20 µl, 0·1 mol l^{-1}) to a solution (2 ml, $1{\cdot}8 \cdot 10^{-5}$ mol l^{-1}) of N-methyl-N-(2,4,6-trinitrophenyl)glycine methyl ester (*II*), a compound with $\lambda_{max} = 400$ nm is formed with the half-life of several seconds (Fig. 1). The rapid formation of this compound is then followed by a slow absorbance decrease in the whole wavelength range measured (330—480 nm). The absorbance decrease is accelerated with increasing methoxide concentration. If a drop of methanolic hydrochloric acid (1 mol l^{-1}) or a drop of methanolic acetate buffer ($[CH_3COOH] = 0{\cdot}8$ mol l^{-1}, $[CH_3COONa] = 0{\cdot}2$ mol l^{-1}) was added to a fresh solution of the compound with $\lambda_{max} = 400$ nm, an abrupt absorbance decrease took place due to protonation, whereupon a slower absorbance change was observed corresponding to formation of a compound with $\lambda_{max} = 385$ nm. The behaviour described is quite analogous to that in the reaction of N-(2,4,6-trinitrophenyl)glycine methyl ester with methoxide, 2-nitroso-4,6-dinitroaniline being formed in the latter case on subsequent acidification[1]. The only difference consists in the fact that the mixture of conjugated base of 2-nitroso-4,6-dinitroaniline and its adducts with methoxide is stable in methoxide solutions.

On the basis of preliminary kinetic experiments in which the conditions for isolation of the product were determined, we carried out an experiment on preparative scale and isolated the chief reaction product in the yield of 57%. The product obtained exhibited identical spectra with those in Fig. 1 (both in acetate buffer and in 10^{-3} mol . l^{-1} sodium methoxide). The main reaction product was identified (by means of its ^1H, ^{13}C, and ^{15}N NMR spectra) as N-methyl-2-nitroso-4,6-dinitroaniline (*III*). The chemical shifts $\delta(^{15}N)$ of all the nitrogen atoms in the molecule were determined by combining three types of measurements: The chemical shift δ(NH) was determined from the spectrum of the non-labelled compound measured with the proton spin decoupling (δ(NH) −290·1). After addition of chromium(III) tris-acetylacetonate to the sample and accumulation of the spectra overnight, the signals of the nitro groups could be found ($\delta(NO_2)$ −14·5 and −16·3). The signal of nitroso group was not found in the spectrum of the non-labelled compound. In the spectrum of the ^{15}N-labelled compound (at the positions 2,6; measured with addition of chromium(III) tris-acetylacetonate) we found the signals with δ 485·0 (NO) and −13·3 (NO_2). The difference in the chemical shift of the nitro group at the position 6 ($\Delta\delta$ = 1·2 ppm) is probably due to concentration effects. The chemical shifts $\delta(^{15}N)$ for N-methyl-2-nitroso-4,6-dinitroaniline (*III*) are very close to the corresponding ones for 2-nitroso-4,6-dinitroaniline[1]. From the chemical shifts $\delta \sim 480$ it is obvious that the compounds really are nitroso compounds and not the isomeric oximes. The NMR spectra of N-methyl-2-nitroso-4,6-dinitroaniline (*III*) were measured in deuteriochloroform, whereas those of 2-nitroso-4,6-dinitroaniline were measured in hexadeuteriodimethyl sulphoxide. N-Methyl-2-nitroso-4,6-dinitroaniline (*III*), dissolved in dimethyl sulphoxide, undergoes a very rapid decomposition accompanied by

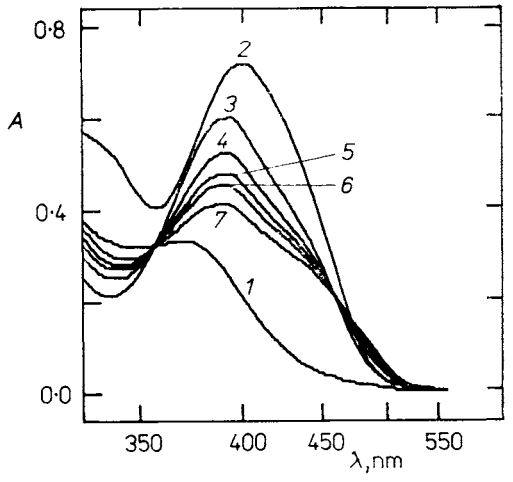
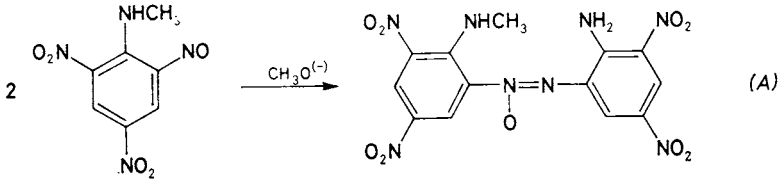


FIG. 1

Electronic spectra of N-methyl-N-(2,4,6-trinitrophenyl)glycine methyl ester in methanol (c = 1·8 . 10^{-5} mol l^{-1}, spectrum *1*), of the mixture of adducts and anion c. 30 s after addition of 20 µl 0·1 mol l^{-1} CH_3ONa (spectrum *2*) and 10 s, 5, 10, 15, and 30 min after addition of 20 µl acetate buffer ([CH_3COOH] = 0·8 mol l^{-1}, [CH_3COONa] = 0·2 mol l^{-1}, spectra *3*—*7*)

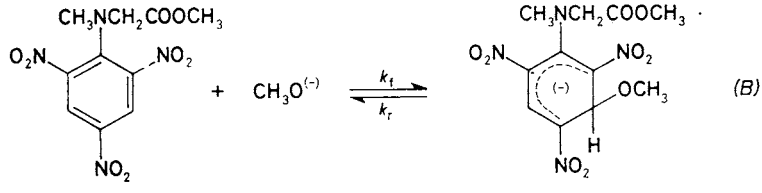
precipitation of the decomposition products; 2-nitroso-4,6-dinitroaniline is insoluble in deuteriochloroform.

In the preparation of N-methyl-2-nitroso-4,6-dinitroaniline (*III*) a red microcrystalline precipitate appears after acidification of the mixture of the anion and adducts, the NMR spectrum of this substance being different from that of the nitroso compound *III*. This red substance is not formed in the reactions followed spectrophotometrically (i.e. at the concentrations of the compounds *II* and *III* below 10^{-4} mol l^{-1}). The ^{13}C NMR spectrum of this compound exhibits twelve signals of aromatic carbon atoms (out of them eight signals of quaternary carbon atoms and 4 signals of CH groups) and one signal of aliphatic carbon atom. The ^{1}H NMR spectrum of this compound shows a doublet of one $NHCH_3$ group and absorptions of four aromatic protons: a doublet with δ 9·67 (1 H) and a narrow multiplet with δ 8·96 (3 H). Addition of deuteriochloroform to the solution of the compound in hexadeuteriodimethyl sulphoxide (the final ratio of the two solvents about 1 : 1) caused a change in the chemical shifts to the following values: 9·83 d, 1 H and 9·06 d, 1 H (J = 2·44 Hz) and 9·04 d, 1 H and 8·81 d, 1 H (J = 2·93 Hz). Hence, both the pairs of protons are at *meta* positions. From these spectral data and from the result of elemental analysis we suggest for the compound the structure of 2-amino-2'--methylamino-3,3',5,5'-tetranitroazoxybenzene (see Eq. (*A*)); an analogous azoxy compound (2-amino-2'-methylamino-5,5'-dinitro-ONN-azoxybenzene) was also isolated from the reaction mixture of N-methyl-N-(2,4-dinitrophenyl)glycine methyl ester and sodium methoxide[4]. In this case the azoxy compound was identified by means of ^{15}N NMR and mass spectra, too.



(*A*)

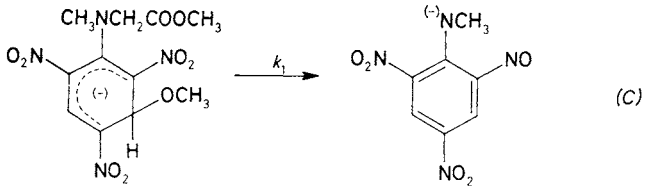
The nitroso compound *III* is stable neither in crystalline state, nor in chloroform solutions, 2-amino-2'-methylamino-3,3',5,5'-tetranitroazoxybenzene, too, being precipitated from chloroform solutions on standing.



(*B*)

II *IV*

The nitroso compound *III* is formed in two (kinetically separated) steps. The first, faster step involves the addition of methoxide to position 3 of ester *II* giving the 1,3-adduct[5] (see Eq. (*B*)), the subsequent step (see Eq. (*C*)) consists in the transformation of the 1,3-adduct (via the aziridinone intermediate and other reactive intermediates) into the nitroso compound *III*. The reaction mechanism of formation of the nitroso compound *III* obviously is similar to that given in Scheme 1 except for the fact that in the case of ester *II* the aziridinone intermediate can only be formed from the 1,3-adduct *IV*.



IV (*C*)

The formation of 1,3-adduct *IV* and nitroso compound *III* is characterized by two relaxation times, τ_1, τ_2, defined[6] by Eq. (*1*)

$$(\tau_{1,2})^{-1} = \tfrac{1}{2}(k_f + k_r + k_1 \pm [(k_f + k_r + k_1)^2 - 4k_f k_1]^{1/2}) . \qquad (1)$$

As the rate constant of the subsequent formation of nitroso compound *III* is substantially smaller than those of formation and decomposition of adduct *IV*, the reactions described by Eqs (*B*), (*C*) can be solved as a rapid pre-equilibrium (*B*) with the rate constant τ_1^{-1} (Eq. (*2*))

$$\tau_1^{-1} = k_f[CH_3O^{(-)}] + k_r \qquad (2)$$

followed by slow transformation of the adduct into the nitroso compound with the rate constant τ_2^{-1} defined in Eq. (*3*)

$$\tau_2^{-1} = k_1 K[CH_3O^{(-)}]/(1 + K[CH_3O^{(-)}]) , \qquad (3)$$

where k_1 means the rate constant of irreversible transformation of adduct *IV* into nitroso compound *III*, and the fraction $K[CH_3O^{(-)}]/(1 + K[CH_3O^{(-)}])$ denotes the molar fraction of the 1,3-adduct *IV* in its mixture with the starting ester *II*. Figure 2 shows the dependence of logarithm τ_2^{-1} of formation of nitroso compound *III* on log $[CH_3O^-]$.

The dependence of the rate constant τ_1^{-1} of the reaction of the starting ester *II* with methoxide on the concentration $[CH_3O^{(-)}]$ was linear in the whole range of

methoxide concentrations investigated (i.e. from $2{\cdot}3 \cdot 10^{-3}$ to $2{\cdot}5 \cdot 10^{-1}$ mol l^{-1}). The rate constants calculated from the slope (k_f) and the intercept (k_r) of the dependence τ_1^{-1} vs $[CH_3O^{(-)}]$ have the following values: $k_f = (415 \pm 30)$ l mol^{-1} s^{-1} and $k_r = (37 \pm 3)$ s^{-1}. The equilibrium constant of formation of the 1,3-adduct *IV*, is $k = k_f/k_r = (11{\cdot}2 \pm 1{\cdot}7)$ l mol^{-1}. Both the rate constants k_f, k_r and the equilibrium constant K have comparable values with those[5] of formation and decomposition of 1,3-adducts of N-alkyl-2,4,6-trinitroanilines. The equilibrium constant of formation of the 1,3-adduct of ester *II* ($K = 11{\cdot}2$ l mol^{-1}) is smaller (by more than one order of magnitude) than the overall equilibrium constants of formation of the conjugated base and 1,3-adduct of methylamide and esters of N-(2,4,6-trinitrophenyl)glycine and -alanine[1,7,8]. The conjugated base by far predominates in the equilibrium mixtures of these compounds, which is in accordance with the fact that the inductive effect of $-CH_2COX$ group more strongly affects the acidity of the proton of the nearer NH group than the addition of methoxide to the more distant position 3 of the trinitrophenyl group.

The comparison of rate constants of formation of the nitroso compound *I* from N-(2,4,6-trinitrophenyl)glycine methyl ester and nitroso compound *III* from N-methyl-N-(2,4,6-trinitrophenyl)glycine methyl ester (*II*) indicates that the nitroso compound *III* is formed from the adduct of ester *II* with methoxide faster than the nitroso compound *I* from the mixture of the conjugated base of the adduct of N-(2,4,6-trinitrophenyl)glycine methyl ester. The rate of formation and the nitroso compound *I* was only measured[1] in 4-bromophenol–sodium 4-bromophenoxide buffers where it is impossible to measure the equilibrium constant of the pre-equilibrium established between the starting substance and methoxide. Therefore, we extended the investigation by the measurement of the reaction rate of N-(2,4,6-trinitrophenyl)glycine

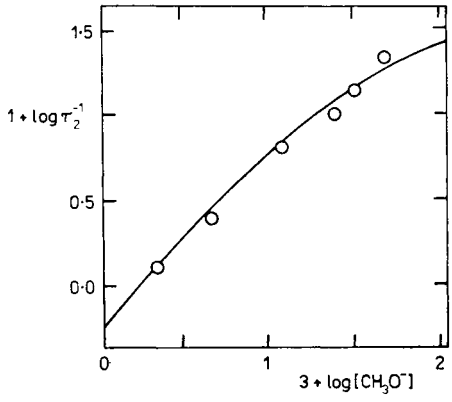
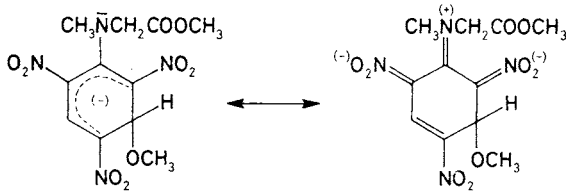


FIG. 2

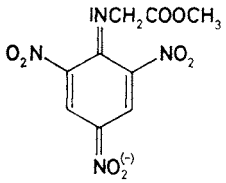
The dependence of logarithm of the rate constant τ_2^{-1} of formation of nitroso compound *III* on log $[CH_3O^{(-)}]$. The full line represents the dependence calculated from Eq. (*3*) with application of the values $K = 11{\cdot}2$ l mol^{-1} and $k_1 = 5{\cdot}0$ s^{-1}

methyl ester with methoxide using the stopped-flow method. The experimental rate constant of formation of the nitroso compound *I* is defined also by Eq. (*2*), but K represents the overall equilibrium constants of formation of the mixture of the conjugated base and the adduct substrate–methoxide, and k_1 is the rate constant of transformation of this mixture into the nitroso compound *I*. By optimization we obtained, from the values of experimental rate constants k according to Eq. (*2*), the values $k_1 = (1{\cdot}6 \pm 0{\cdot}2)\,s^{-1}$ and $K = (150 \pm 30)\,l\,mol^{-1}$. The constants corresponding to the reaction of ester *II* have the following values: $k_1 = 5{\cdot}0\,s^{-1}$ and $K = 11{\cdot}2\,l\,mol^{-1}$. The comparison of the equilibrium constants K shows that N-(2,4,6-trinitrophenyl)glycine methyl ester reacts with methoxide to give, predominantly, the conjugated base, whereas the 1,3-adduct is probably formed in the yields below 10%. Hence, it can be presumed that in this case the nitroso compound *I* is predominantly formed by the transformation of the conjugated base. The rate constant of this reaction is three times smaller than that of formation of the nitroso compound *III* from the 1,3-adduct of ester *II*, although in the latter case the formation of the aziridinone intermediate must involve an electron pair which is a part of a delocalized system (Scheme 2). Therefrom it follows that for the formation of the



SCHEME 2

nitroso compounds *I* and *III* decisive are stereoelectronic effects, and the attack of the carboxylic carbon atom by the nitrogen electron pair located predominantly in

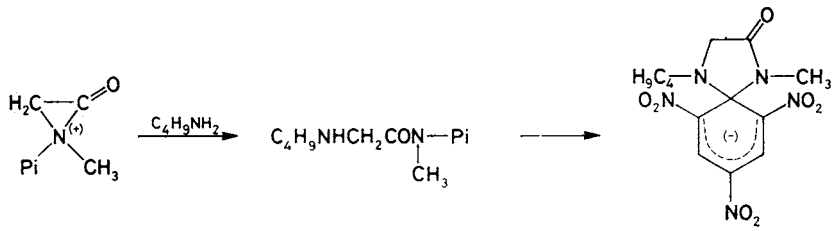


V

a *p* orbital of the system in Scheme 2 is more favourable than the attack by the nitrogen electron pair located predominantly in an sp^2 orbital of the species *V*.

In an extreme case it can be supposed that also the reaction of N-(2,4,6-trinitrophenyl)glycine methyl ester produces the nitroso compound *I* only via the 1,3-adduct and not through the conjugated base. In such a case, however, the rate constant of the transformation of 1,3-adduct into nitroso compound *I* should have a considerably high value of $k_1 = 15$ to $20\ s^{-1}$.

The formation of nitroso compound *III* from ester *II* was also followed in the presence of butylamine ($1\ mol\ l^{-1}$) and in the butylamine–butylammonium chloride buffer ($[C_4H_9NH_2] = 1\ mol\ l^{-1}$, $[C_4H_9NH_2]/[C_4H_9NH_3Cl] = 100$). Aziridinone derivatives react with negatively charged nucleophilic agents at the carbonyl carbon atom and with neutral nucleophiles at α-carbon atom[9]. If the intermolecular attack by butylamine competed against the intramolecular attack of CH_2 group of aziridinone cycle by oxygen atom of nitro group, then compound *V* would be formed which would be immediately cyclized to spiro adduct *VI* in the given medium (Scheme 3). The spiro adduct *VI* could be determined spectrophotometrically, if it



Pi = 2,4,6-trinitrophenyl

VI

SCHEME 3

were formed in an amount of at least 1% of the original concentration of ester *II*, however, its formation was never proved in the experiments described. This means that the "effective molarity"[10] of the nitro group (in the nucleophilic attack at the α-carbon atom of the aziridinone) is at least by two orders of magnitude higher as compared with butylamine.

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Translated by J. Panchartek.